EFFECT OF TYPE OF ACID AND TIME BETWEEN ACIDIFICATION AND RESIN CONTACT ON THE REMOVAL OF RADIOSTRONTIUM FROM MILK

Acidification increases the removal of radiostrontium from milk by ion exchange (2, 5). Citric acid has been used by previous workers for this purpose, the acid being added to milk in a beaker or vat from a buret, or by similar means. Such batch acidification, which results in a gradual lowering of the pH, is not compatible with present-day continuous commercial processing. A continuous, rapid acidification method would be more practical for commercial operations. However, with continuous processing, the the time interval between acidification and resin contact is much less than that occurring when batch acidification is used. It was thought that a shorter holding time might result in lower strontium removal.

It was the purpose of these studies to determine the effect of: (1) the type of acid used for milk acidification, and (2) the time interval between acidification and resin contact on the removal of radiostrontium from milk.

The four acids investigated were acetic, citric, hydrochloric, and phosphoric. The studies related to the time during which the milk was in the acidified condition (following continuous acidification) included the range from 0.5 to 60 min.

EXPERIMENTAL PROCEDURES

Acid-type study. Milk labeled in vivo with strontinum 85, as previously described (3), was divided into four equal lots. The pH of each lot was lowered to 5.3 with a 0.75 N solution of either acetic, citric, hydrochloric or phosphoric acid. Portions of each lot were acidified periodically so as to allow approximately 30 min between acidification and passage through the resin column. A total of 2.5 liters of each lot were passed through separate ion exchange columns containing 100 ml of a cation resin (Amberlite IR-120)[1] at a flow rate of 0.25 resin bed volumes (rbv) per minute. The resin had been previously regenerated with a mixed solution of $CaCl_2$, KCl, $MgCl_2$, and NaCl (4).

Samples were taken from each lot of milk before resin contact, and from each successive five-bed-volume fraction (500 ml) of treated milk. Duplicate samples from each fraction were assayed for strontium 85 with single channel gamma analyzer, utilizing a well-type NaI (thallium-activated) crystal (1). The experiment was repeated and the average of the trials are reported as a per cent of the strontium removed.

[1] Reference to certain products or companies does not imply an endorsement by the Department over others not mentioned.

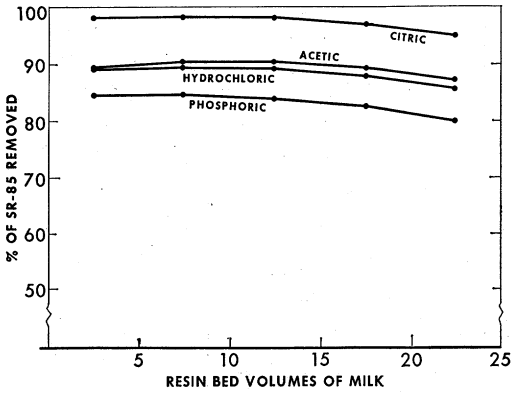

FIG. 2. Comparison of acids used to acidify milks with respect to their effect on strontium removal by ion exchange.

Continuous acidification studies. Milk labeled in vivo with strontium 85 was adjusted to a pH of approximately 5.4 by injecting a 0.75 M solution of citric acid into a continuous flow of milk. The milk flow rate was 400 ml per minute. This required about 5.5 ml of the acid solution. To maintain an accurate and uniform flow of acid at this low rate, the apparatus shown in Figure 1 was used. After filling the citric acid supply cylinder, the system was closed and pressure applied from the nitrogen cylinder. The acid entered the milk stream through a small hypodermic needle, as shown in the Figure. The milk was pumped through a larger needle with a positive pressure metering pump. Approximately 10 psi of pressure were used to inject the acid into the milk stream at the desired rate. This procedure effected rapid mixing. An arrangement for collecting the acidified milk (pH $= 5.42 \pm .05$) was made so that aliquot samples could be held for 0.5, 7.5, 15, 30, and 60 min before passing through the resin columns. Each of the five columns contained 200 ml of cation resin, prepared as described above. The milk flow rate through the columns was 50 ml per minute (0.25 rbv/min). Six fractions of 2.5 rbv each were collected for Sr^{85} removal analysis.

The milk for the shortest holding time (0.5 min) passed directly through Resin Column I.

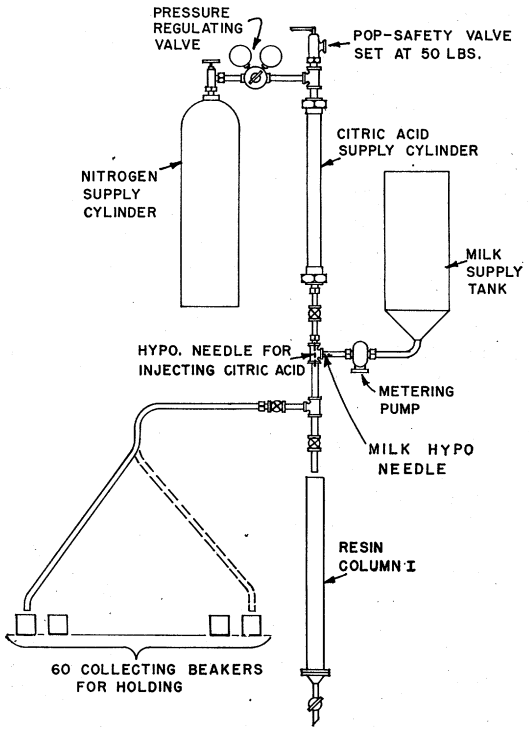

FIG. 1. Schematic drawing of the apparatus used for continuous milk acidification.

It was intended that the time interval between acidification and resin contact for this portion would be kept at a minimum. However, due to the volume of the connecting lines, there was a delay of about 30 sec. Only enough milk was maintained above the resin level to keep air from getting into the column.

The remaining portion of the milk was collected in a series of 60 beakers, each of which contained the quantity collected during a 1-min interval (350 ml). Fifty-milliliter portions were withdrawn from each beaker after 7.5-, 15-, 30-, and 60-min holding times and passed through Resin Columns II, III, IV, and V, respectively. The samples were passed through the columns in the order in which they were collected, thereby approximating continuous holding times as specified above.

RESULTS AND DISCUSSION

Figure 2 shows the percentage of strontium removed for the four types of acids studied. The average removals for the 25 bed volumes were 97.5, 89.4, 88.4, and 83.1 for citric, acetic, hydrochloric, and phosphoric, respectively. Analysis of the data by the Duncan's Multiple Range test shows a highly significant advantage for the citric acid over the three other acids, with phosphoric being the least effective. The lower removal obtained with phosphoric acid may be explained by the low solubility of the strontium phosphates and by the tendency of the alkaline earths to combine as phosphocaseinates, making these ions less available for cation exchange. The net charge of the complex is negative, even at a pH as low as 5.3. It has been shown that about 15% of the strontinum is colloidally bound at a pH of 5.2 when citric acid was used for acidification (3). It is probable that a greater amount is complexed when phosphoric acid is used for acidifying. Since there is little or no calcium and strontium complexing by the acetic and hydrochloric acids, these ions would, therefore, be more available for exchange. The greater removal obtained with citric acid than with acetic and HCl acids is probably related to its chelating effectiveness for divalent ions. Citrate may form complexes with alkaline earths having a net positive charge at the pH values employed.

The results of the holding-time studies following continuous acidification are shown in Table 1. A small but definite increase in the amount of strontium removed resulted when the holding time after acidification was increased from 0.5 to 60 min. Results of Duncan's Multiple Range test show a significant difference between the average removal for each of the holding times. These differences may be the result of the time required for caseinate micelle dispersion, and of the rate of strontium citrate chelation following acidification. In any case, it appears that several minutes are required for some of the strontium ions, combined with the caseinate complex, to become available for ion exchange.

In relating these results to practical operations, the milk transit time through the resin column must be considered. Flow rates through a column from 0.06 to 0.12 rbv per minute are considered to be practical (1). These rates correspond to transit times in the resin bed of approximately 6 and 3 min, respectively. In

TABLE 1

Effect of milk holding time after acidification on the removal of strontium from milk

2½ Bed volume milk fraction	Per cent of strontium removed from milk				
	Holding time[a]				
	0.5 min	7.5 min	15 min	30 min	60 min
1	92.8	93.1	93.9	95.2	95.3
2	91.1	91.9	92.8	93.6	94.3
3	91.0	91.5	92.6	93.3	94.4
4	90.8	91.3	92.6	93.4	94.5
5	86.9	88.9	90.6	91.4	92.0
6	86.7	87.7	88.6	89.8	90.6
Avg	89.9	90.7	91.9	92.8	93.5

[a] Exclusive of milk transit time through resin column.

addition, a time delay of a few minutes would occur in the headspace above the resin. Therefore, under normal continuous operations, a holding-time after acidification of several minutes may be expected. Under most operating conditions the increase in strontium removal gained by longer holding times (60 min compared to normal continuous transit times) is not considered of enough importance to necessitate provisions for a longer holding time.

In addition to being more suitable for commercial operations, continuous acidification offers the advantage of less chance of localized protein precipitation than the batch method. This procedure of mixing the acid with milk may have application in other areas of specialized dairy processing, such as in current trends involving the production of sour cream, cottage cheese, cream cheese, and yoghurt.

SUMMARY

Acetic, citric, hydrochloric, and phosphoric acids were used to lower the pH of milk (in vivo labeled with strontium 85) to 5.3. The milks were then passed through cation exchange columns and the per cent strontium removal determined. The use of citric acid effected 97.5% removal from 25 resin bed volumes of milk compared to 89.4, 88.4, and 83.1% for acetic, hydrochloric, and phosphoric acids, respectively.

Results of studies carried out to determine the effect of time between acidification and resin contact on strontium removal, using citric acid for acidifying, showed that there was a small increase in the percentage removal with increasing holding time.

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REFERENCES

(1) EASTERLY, D. G., HARRIS, J. Y., BUNCE, L. A., AND EDMONDSON, L. F. Factors Affecting the Removal of Radiostrontium from Milk by Ion Exchange Resins. J. Dairy Sci., 46: 1207. 1963.

(2) EDMONDSON, L. F., KEEFER, D. H., DOUGLAS, F. W., JR., HARRIS, J. Y., AND DODSON, E. The Removal of in Vivo and in Vitro Labeled Radiostrontium from Milk and Its Distribution Between Centrifugally Separated Phases. J. Dairy Sci., 44: 1166. 1961.

(3) EDMONDSON, L. F., KEEFER, D. H., DOUGLAS, F. W. JR., HARRIS, J. Y., AND DODSON, E. Comparison of the Removal of Radiostrontium from in Vivo and in Vitro Labeled Milk by Ion Exchange Resins. J. Dairy Sci., 46: 1362. 1963.

(4) LANDGREBE, A. R., EDMONDSON, L. F., AND DOUGLAS, F. W., JR. Optimum Ratio of Cations on Nuclear Sulfonic Acid Resin for Minimum Change in Composition of Resin-Treated Milk, J. Dairy Sci., 46: 181. 1963.

(5) MURTHY, G. K., MASUROVSKY, E. B., CAMPBELL, J. E., AND EDMONDSON, L. F. Method for Removing Cationic Radionuclides from Milk. J. Dairy Sci., 44: 2158. 1961.